# Einstein's theory of Lattice Heat Capacity

In 1911, Einstein resolved the discrepancies of the classical theory of specific heat by applying the Planck's quantum theory. Einstein retained all the assumptions of the classical theory except replacing the classical harmonic oscillator by quantum harmonic oscillators which can have only discrete energy values. The main assumptions of Einstein theory were as follows:-

1. The atoms of a crystal are regarded as identical and independent harmonic oscillators.
2. A solid having N atoms is equivalent to having 3N one-dimensional harmonic oscillators.
3. Due to identical enviroment each oscillator vibrates with the same natural frequency $\omega$.
4. As the oscillators are quantum ~~mechanical~~ oscillators, they can have discrete energy spectrum.
5. Any quantum state can have any no. of oscillation.
6. Atomic oscillators are distingeishable and obey Maxwell-Boltzmann distribution law of energy due to their location at separate sites.

Considering the Planck's quantum theory, the discrete energy values of an oscillator with frequency $\nu$ are given by,

$$E = nh\nu = n\hbar\omega \quad \text{---------- (1)}$$

where, $n = 0, 1, 2, 3, \ldots$ called the quantum number.

Using wave mechanical consideration, the energy of a harmonic oscillator is,

$$E_n = (n+1/2)\hbar\omega_0 = (n+1/2)\hbar\omega_0 \quad \text{--- (2)}$$

Here $\frac{1}{2}\hbar\omega_0$ is the zero-point energy contribution to the internal energy of the oscillator.

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Now the average energy of an oscillator is given by,

$$\langle E \rangle = \frac{\sum_{n=0}^{\infty} E_n e^{-E_n/k_B T}}{\sum_{n=0}^{\infty} e^{-E_n/k_B T}}$$

$$= \frac{\sum_{n=0}^{\infty} (n+1/2)\hbar\omega_0 e^{\{-(n+1/2)\hbar\omega_0/k_B T\}}}{\sum_{n=0}^{\infty} e^{\{-(n+1/2)\hbar\omega_0/k_B T\}}}$$

$$\langle E \rangle = \frac{\hbar\omega_0 \sum_{n=0}^{\infty} (n+1/2) e^{(-(n+1/2)x}}{\sum_{n=0}^{\infty} e^{(n+1/2)x}}$$

where, $x = -\hbar\omega_0/k_B T$

$$\therefore \langle E \rangle = \frac{\hbar\omega_0 (1/2 e^{x/2} + 3/2 e^{3/2 x} + 5/2 e^{5/2 x} + \cdots)}{(e^{x/2} + e^{3x/2} + e^{5/2 x} + \cdots)}$$

$$= \hbar\omega_0 \frac{d}{dx} \ln (e^{x/2} + e^{3/2 x} + e^{5/2 x} + \cdots)$$

$$= \hbar\omega_0 \frac{d}{dx} \ln [e^{x/2}(1 + e^{x} + e^{2x} + \cdots)] \quad \text{---(2)}$$

But $\ln (1 + e^{x} + e^{2x} + \cdots) = -\ln (1 - e^{+x})$

$$\Rightarrow \langle E \rangle = \hbar\omega_0 \frac{d}{dx} [\ln e^{x/2} + \ln (1 + e^{x} + e^{2x} + \cdots)]$$

$$= \hbar\omega_0 \frac{d}{dx} [x/2 - \ln (1 - e^{x})]$$

$$= \hbar\omega_0 \left[1/2 - \frac{1}{1 - e^{x}} (-e^{x})\right]$$

$$= \hbar\omega_0 \left[1/2 + \frac{e^{x}}{1 - e^{x}}\right]$$

$$= \hbar\omega_0 \left[1/2 + \frac{1}{e^{-x} - 1}\right]$$

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$$\Rightarrow \langle E \rangle = \hbar\omega_0 \left[ \frac{1}{2} + \frac{1}{e^{\hbar\omega_0/k_B T} - 1} \right] \quad \left[ \because x = \frac{-\hbar\omega_0}{k_B T} \right]$$

$$\Rightarrow \langle E \rangle = \frac{1}{2}\hbar\omega_0 + \frac{\hbar\omega_0}{e^{\hbar\omega_0/k_B T} - 1} \quad \text{---- (4)}$$

If eqn (1) is used in eqn (4), the expression for the average energy becomes,

$$\langle E \rangle = \frac{\hbar\omega_0}{e^{\hbar\omega_0/k_B T} - 1} \quad \text{---- (5)}$$

From eqn (4) it is clear that for $T \to 0$, $\langle E \rangle = \frac{1}{2}\hbar\omega_0$. This means that atoms are having vibrational energy $\frac{1}{2}\hbar\omega_0$ even at $T = 0$. Since $\frac{1}{2}\hbar\omega_0$ is temp. independent, it has no contribution to specific heat of solids.

Thus the internal energy is,

$$E = 3N\langle E \rangle$$

$$= \frac{3}{2} N\hbar\omega_0 + \frac{3N\hbar\omega_0}{e^{\hbar\omega_0/k_B T} - 1} \quad \text{---- (6)}$$

∴ Molar specific heat of the solid is,

$$C_V = \left( \frac{dE}{dT} \right)_V$$

$$= 3N\hbar\omega_0 \frac{1}{(e^{\hbar\omega_0/k_B T} - 1)^2} \cdot e^{\hbar\omega_0/k_B T} \cdot \left( \frac{\hbar\omega_0}{k_B T^2} \right)$$

$$\Rightarrow C_V = 3Nk_B \left( \frac{\hbar\omega_0}{k_B T} \right)^2 \frac{e^{\hbar\omega_0/k_B T}}{\left( e^{\hbar\omega_0/k_B T} - 1 \right)^2} \quad \text{---- (7)}$$

Let $\Theta_E = \frac{\hbar\omega_0}{k_B}$ known as the characteristics temp or Einstein's temperature.

$$\therefore C_V = 3Nk_B \left( \frac{\Theta_E}{T} \right)^2 \frac{e^{\Theta_E/T}}{\left( e^{\Theta_E/T} - 1 \right)^2} \quad \text{---- (8)}$$

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Now we consider the following cases:

① When the temp. is high: For $T \to$ higher value

$$k_B T \geq \hbar\omega_0 \text{ or } T \geq \frac{\hbar\omega_0}{k_B} \text{ or } T \geq \Theta_E$$

We get, $e^{\hbar\omega_0/k_B T} - 1 = 1 + \frac{\hbar\omega_0}{k_B T} + \cdots - 1 \simeq \frac{\hbar\omega_0}{k_B T}$

Eqn (6) reduces to.

$$\langle E \rangle = \tfrac{1}{2}\hbar\omega_0 + \frac{\hbar\omega_0}{\hbar\omega_0/k_B T}$$

$$= \frac{\hbar\omega_0}{2} + k_B T \simeq k_B T$$

Thus at high temp. the avg. energy $\langle E \rangle$ is the same as that obtained from classical theory.

Now from eqn (7),

$$C_V = \left(\frac{dE}{dT}\right)_V = 3Nk_B \left(\frac{\hbar\omega_0}{k_B T}\right)^2 \frac{\left(1 + \frac{\hbar\omega_0}{k_B T}\right)}{\left(\frac{\hbar\omega_0}{k_B T}\right)^2}$$

$$\simeq 3Nk_B \left(1 + \frac{\hbar\omega_0}{k_B T}\right)$$

At $T \to \infty$, $C_V \to 3Nk_B = 3R$

This is Dulong-petit's law as obtained from classical theory.

② When the temp. is low: For $T \to 0$

$$k_B T \leq \hbar\omega_0 \text{ or } T \leq \frac{\hbar\omega_0}{k} \leq T \leq \Theta_E$$

$$\therefore e^{+\hbar\omega_0/k_B T} - 1 \simeq e^{+\hbar\omega_0/k_B T}$$

From eqn (4), $\langle E \rangle = \tfrac{1}{2}\hbar\omega_0 + \hbar\omega_0 e^{-\hbar\omega_0/k_B T}$

This shows that the avg. energy decreases exponentially with temp. in the low temp. region.

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$$\therefore C_V = \left(\frac{dE}{dT}\right)_V = 3NK_B\left(\frac{\hbar\omega_E}{K_BT}\right)^2 e^{-\hbar\omega_E/K_BT}$$

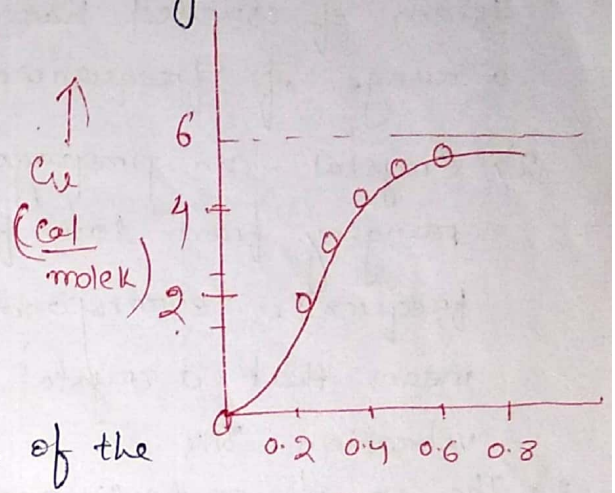
or $$C_V = 3NK_B\left(\frac{\Theta_E}{T}\right)^2 e^{-\Theta_E/T}$$

Hence for $T \leq \Theta_E$,

$$C_V \propto e^{-\Theta_E/T}$$

This shows rapid decrease in $C_V$ with the decrease of T. For most of the solid $C_V$ is found to vary as $T^3$.

Though Einstein's theory agrees well with expt. over a wide range of temp., it shows a more rapid decrease of $C_V$ than the observed decrease in $C_V$.




## Drawbacks of Einstein's theory

Einstein assumed that each atom of the solid vibrates as a single unit independent of it's neighbours. The vibrational motion of the crystal as a whole was considered to be the same as the vibrational motion of a single atom. For this reason all the atoms of the solid were assumed to vibrate with a common frequency ω, the frequency of a single atom. This assumption is over-simplified since the atoms in a crystal are bound together to form a system of couple oscillator which cannot vibrate independently. Actually a solid is capable of vibrating elastically in many different modes.

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# Debye's Theory of Specific Heat of Solids

In 1912, Debye modified Einstein's theory of specific heat of solids on the basis of the following assumptions:-

~~1) The vibrational motion of the system of coupled harmonic oscillators~~

1) The vibrational motion of the crystal as a whole was considered to be equivalent to the vibrational motion of a system of coupled harmonic oscillators which can propagate a range of frequencies rather than a single frequency.

2) Crystal can propagate elastic waves of wavelengths ranging from low frequencies (sound waves) to high frequencies corresponding to infrared absorption. This means that a crystal can have a no. of modes of vibration.

3) The no. of modes (vibrational) per unit frequency range is called density of modes, $Z(\nu)$. The density of vibrational modes of crystal ~~treat~~ can be determined by treating it as a continous medium.

## Density of modes

Consider a one-dimensional continous string of length $L$, fixed at both ends. Let $x$ be the position of a line element and $u(x,t)$ it's displacement from the mean position at any time $t$. Then equation of motion of the string is,

$$\frac{\partial^2 u}{\partial x^2} = \frac{1}{v_s^2}\frac{\partial^2 u}{\partial t^2} \quad \longleftarrow (1)$$

where, $v_s$ = velocity of the wave in the string.

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Since the string is fixed at $x=0$ and $x=L$, eqn (1) represents a standing wave having solution of the type,

$$u(x,t) = A \sin\left(\frac{n\pi x}{L}\right) \cos 2\pi\nu_n t \quad \text{—— (2)}$$

where, $n$ is a positive number and $\geq 1$.

Since the length $L$ of the string is an integral multiple of half wavelengths. i.e. substituting eqn (2) in eqn (1) we get,

$$\lambda_n = \frac{2L}{n} \Rightarrow L = n\frac{\lambda_n}{2} \quad \text{—— (3)}$$

and the frequency, $\nu_n = \frac{v_s}{\lambda_n} = \frac{n v_s}{2L}$ —— (4)

Thus, the frequency $\nu$ has discrete values i.e.

$$\nu_1 = \frac{v_s}{2L}, \nu_2 = \frac{v_s}{L}, \nu_3 = \frac{3v_s}{2L}, \ldots$$

This shows that the frequency of the string can have discrete values only and it's an integral multiple of $\frac{v_s}{2L}$. It implies that the frequency spectrum of a continous string is discrete and contains an $\infty$ no. of parallel lines equidistant from each other.

From, eqn (4), $n = \frac{2L}{v_s}\nu_n$

$$\therefore \boxed{d_n = \frac{2L}{v_s} d\nu} \quad \text{—— (5)}$$

Here $d_n$ represents the possible mode of vibration in the frequency interval $d\nu$.

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## Three-dimensional Case

Now considering the 3-dimensional case, the wave eqn can be written as,

$$\frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} + \frac{\partial^2 u}{\partial z^2} = \frac{1}{v_s^2} \frac{\partial^2 u}{\partial t^2} \quad \text{---- (6)}$$

Assuming the 3-dimensional continous medium as a cube of side L, with fixed faces, the standing wave soln of eqn (6) is,

$$u(x,y,z,t) = A \sin\left(\frac{n_x \pi x}{L}\right) \sin\left(\frac{n_y \pi y}{L}\right) \sin\left(\frac{n_z \pi z}{L}\right) \cos(2\pi \nu_n t) \quad \text{---- (7)}$$

where, $n_x, n_y, n_z$ are positive integers $\geq 1$.

Differentiating eqn (7) twice w.r.t x, y and z we get,

$$\frac{\partial^2 u}{\partial x^2} = -\left(\frac{n_x \pi}{L}\right)^2 u(x,y,z,t)$$

$$\frac{\partial^2 u}{\partial y^2} = -\left(\frac{n_y \pi}{L}\right)^2 u(x,y,z,t)$$

and $$\left(\frac{\partial^2 u}{\partial z^2}\right) = -\left(\frac{n_z \pi}{L}\right)^2 u(x,y,z,t)$$

Substituting these values in eqn (7), we get

$$\left(\frac{n_x \pi}{L}\right)^2 + \left(\frac{n_y \pi}{L}\right)^2 + \left(\frac{n_z \pi}{L}\right)^2 = \frac{1}{v_s^2} 4\pi^2 \nu^2 = \frac{4\pi^2}{\lambda^2}$$

$$\Rightarrow n_x^2 + n_y^2 + n_z^2 = \frac{4\pi^2}{\lambda^2} \times \frac{L^2}{\pi^2} = \frac{4L^2 \nu^2}{v_s^2} \quad \text{---- (8)}$$

Eqn (8) gives the possible modes of vibration, where $n_x, n_y, n_z$ determine possible frequencies or wavelengths.

Now we considering a network of points in the space defined by 3 positive integral co-ordinates $n_x, n_y$ and $n_z$. The radius vector R of any point from the origin is,

$$R^2 = n_x^2 + n_y^2 + n_z^2 = \frac{4L^2 \nu^2}{v_s^2} \quad \text{---- (9)}$$

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$n'(q)$ represents a sphere of vol.

$$V' = \frac{4}{3}\pi R^3$$

$$\therefore dV' = 4\pi R^2 dR$$

The no. of modes in the frequency range $\nu$ to $\nu+d\nu$ is equal to the no. of points in the spherical shell b/w volumes $V'$ and $V'+dV'$ or in the range $R$ to $R+dR$ of the radius vector is,

$$dn = 4\pi R^2 dR$$

Since a mode of vibration is determined by the numbers $n_1, n_2$ which are $\geq 1$, we shall consider the points lying in the first octant only. Hence, the no. of possible modes of vibration $Z(\nu)d\nu$ in the frequency interval $\nu$ to $\nu+d\nu$ is given by,

$$Z(\nu)d\nu = \frac{1}{8} \times 4\pi R^2 dR.$$

$$= \frac{1}{8} \times 4\pi \frac{4L^2\nu^2}{v_s^2}\frac{2L}{v_s} d\nu$$

$$= \frac{4\pi L^3 \nu^2}{v_s^3} d\nu = \left(\frac{4\pi V}{v_s^3}\right)\nu^2 d\nu \quad \text{——— (10)}$$

where, $V = L^3$, the vol. of the cube

But the elastic waves propagating in solid are of two types viz transverse waves and longitudinal waves with velocity of propagation $v_l$ and $v_t$ respectively.

$$\therefore Z(\nu)d\nu = 4\pi V\left(\frac{2}{v_t^3} + \frac{1}{v_l^3}\right)\nu^2 d\nu \quad \text{——— (11).}$$

*[Since each point occupies on an average, a unit vol. in the space of integers, the no. of points present in the vol. $dV'$ of the spherical shell is numerically equal to the vol. of the shell i.e. $dn = 4\pi R^2 dR$]

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# The Debye Approximation

If the interatomic distance is small as compared to the wavelength of elastic waves, the crystal can be regarded as a continuum from the pt. view of the wave. Based on this idea, Debye assumed that the continuum model is applicable to all possible vibrational modes of the crystal. If the solid contains N(finite) no. of atoms, then the total no. of vibrational mode is limited to 3N. This puts an upper limit to the frequency of the elastic wave which can propagate through the crystal and is called the Debye frequency $\nu_D$. Hence, the frequency spectrum of a continous medium is cut off at $\nu_D$. It is Thus common to transverse and longitudinal modes of vibration. Thus, Debye frequency can be determined by equating the total no. of possible frequency to 3N.

$$\therefore \int_0^{\nu_D} Z(\nu)\, d\nu = 3N$$

$$\Rightarrow \int_0^{\nu_D} 4\pi V \left(\frac{2}{v_t^3} + \frac{1}{v_l^3}\right) \nu^2 d\nu = 3N$$

$$\Rightarrow 4\pi V \left(\frac{2}{v_t^3} + \frac{1}{v_l^3}\right) \frac{\nu_D^3}{3} = 3N$$

$$\Rightarrow \nu_D^3 = \frac{9N}{4\pi V} \left(\frac{2}{v_t^3} + \frac{1}{v_l^3}\right)^{-1} \quad \text{——— (12)}$$

The vibrational energy of a crystal is determined by using the Planck's theory. The average energy of an oscillator having frequency $\nu$ at a temp. T is given by,

$$\langle E \rangle = \frac{h\nu}{e^{h\nu/kT} - 1} \quad \text{——— (13)}$$

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The vibrational energy of the crystal is,

$$E = \int_0^{\nu_D} \langle E \rangle Z(\nu)\, d\nu$$

$$= \int_0^{\nu_D} 4\pi V \left(\frac{2}{v_t^3} + \frac{1}{v_l^3}\right) \frac{h\nu^3}{e^{h\nu/K_BT} - 1} d\nu$$

$$= 4\pi V h \left(\frac{2}{v_t^3} + \frac{1}{v_l^3}\right) \int_0^{\nu_D} \frac{\nu^3 d\nu}{e^{h\nu/K_BT} - 1}$$

$$\Rightarrow E = \frac{9Nh}{\nu_D^3} \int_0^{\nu_D} \frac{\nu^3 d\nu}{e^{h\nu/K_BT} - 1} \quad \text{[From eq}^n (12)\text{]}$$

Now putting, $\frac{h\nu}{K_BT} = x$ and $\frac{h\nu_D}{K_BT} = x_m$

we have, $\nu = \frac{x K_B T}{h}$ and $\Rightarrow d\nu = \frac{K_B T}{h} dx$

Hence, $$E = \frac{9Nh}{\nu_D^3} \left(\frac{K_BT}{h}\right)^4 \int_0^{x_m} \frac{x^3 dx}{e^x - 1}$$

$$= 9N \left(\frac{K_BT}{h\nu_D}\right)^3 K_BT \int_0^{x_m} \frac{x^3\, dx}{e^x - 1}$$

$$\Rightarrow E = 9NK_BT \left(\frac{T}{\theta_D}\right)^3 \int_0^{\theta_D/T} \frac{x^3\, dx}{e^x - 1} \quad \text{——— (14)}$$

where, $\theta_D = \frac{h\nu_D}{K}$ is called Debye temperature.

Now the specific heat at const. vol. is,

$$C_V = \left(\frac{dE}{dT}\right)_V = 9NK_B \left(\frac{T}{\theta_D}\right)^3 \int_0^{\theta_D/T} \frac{e^x x^4}{(e^x - 1)^2} dx \quad \text{——— (15)}$$

$$= 3R \left(\frac{\theta_D}{T}\right) F_D \quad (\text{for } N = N_A)$$

where, the funcn $F_D$ is called the Debye's function and is given by, $F_D = 3\left(\frac{T}{\theta_D}\right)^3 \int_0^{\theta_D/T} \frac{e^x x^4}{(e^x - 1)^2} dx$

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Special case:- Now considering the following cases!

1. When the temp. T is high: For $T \geq \theta_D$, $x = \frac{\theta_D}{T}$ is comparable to unity.

So, $e^x - 1 \simeq 1 + x + \frac{x^2}{2} + \cdots - 1 \simeq x$

∴ From eqn (14),

$$E = 9NK_BT\left(\frac{T}{\theta_D}\right)^3 \int_0^{\theta_D/T} \frac{x^3\,dx}{x}$$

$$= 9NK_BT\left(\frac{T}{\theta_D}\right)^3 \int_0^{\theta_D/T} x^2\,dx$$

$$= 3NK_BT\left(\frac{T}{\theta_D}\right)^3 \cdot \left(\frac{\theta_D}{T}\right)^3$$

$$\Rightarrow E = 3NK_BT$$

$$\therefore C_v = \left(\frac{dE}{dT}\right)_V = 3NK = 3R \quad \text{---------- (16)}$$

Thus at high temp., the Debye's theory obeys the Dulong and petit's law.

2. When the temp. T is low:- For $T \leq \theta_D$, $x_m = \frac{\theta_D}{T} \to \infty$

Hence eqn (14) reduces to,

$$E = 9NK_BT\left(\frac{T}{\theta_D}\right)^3 \int_0^{\infty} \frac{x^3\,dx}{e^x - 1}$$

$$= 9NK_BT\left(\frac{T}{\theta_D}\right)^3 \cdot \frac{\pi^4}{15} \quad \left[\because \int_0^{\infty} \frac{x^3\,dx}{e^x - 1} = \frac{\pi^4}{15}\right]$$

$$\Rightarrow E = \frac{3}{5}\pi^4 NK_B \frac{T^4}{\theta_D^3} \quad \text{--- (17)}$$

Eqn (17) shows that the vibrational energy of the crystal is proportional to $T^4$ which is analogous to Stefan's law of black body radiation.

Now $C_v = \left(\frac{dE}{dT}\right)_V = \frac{12}{5}\pi^4 NK\left(T/\theta_D\right)^3 = \frac{12}{5}\pi^4 R\left(\frac{T^3}{\theta_D^3}\right)$

Thus at very low temp., the sp. heat is proportional to $T^3$. This is called Debye's $T^3$ law and holds for $T \leq \frac{\theta_D}{10}$.

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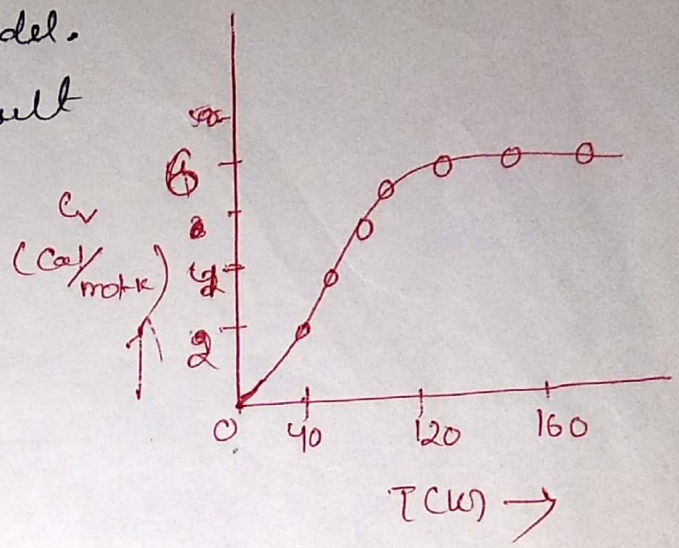
Debye law is applicable to explain experimental results with excellent agreement. i.e. matching of the experimentally determined values of the sp heat at various temp. with those calculated theoritically using the Debye's model.

Figure shows the experimental result for silver at $\Theta_D = 225\ K$.

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